Water Quality Criteria/Standards: *International Trends and Applications*

W.A. Stubblefield

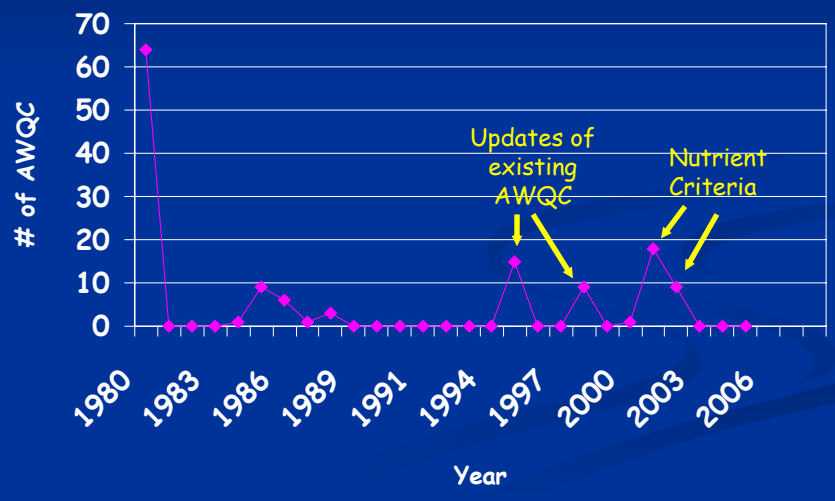
Agenda

- USA AWQC status
- International perspectives
  - PNECs
  - BLM
- New data drivers
  - REACH
- Examples
  - Co and Mn
- Future directions

Statutory Authority for Water Quality Criteria

- Section 304(a)(1) … EPA shall develop and publish criteria for water quality that accurately reflect the latest scientific knowledge on all identifiable effects on health and welfare to plankton, fish, shellfish, wildlife, plant life, shorelines, beaches, esthetics, recreation, biological community diversity, productivity, and stability…

AWQC in the USA



So what's new from HQ regarding AWQC…

- Biotic Ligand Models (BLM)
- Emerging Contaminants (including EDCs and PPCPs) Exploration of "screening criteria/values"
- Incorporation of data for non-traditional endpoints and organisms

Water Quality Criteria around the world

A rose by an other name…

- Ambient water quality criteria (AWQC)
- Canadian water quality guidelines (WQG)
- Predicted no effect concentrations (PNEC)
- Australian trigger values
- OECD Maximum tolerable concentrations (MTC)
- Etc.

Numerical criteria/standards

- Values derived are scientifically-based numbers which are intended to protect aquatic life from the adverse effects of contaminants without consideration of defined water body uses, societal values, economics, or other non-scientific considerations.

Water quality policies differ globally

- EU's Water Framework Directive
  - Policy is intended to "…contribute to pursuit of the objectives of preserving, protecting, and improving the quality of the environment, in prudent and rational utilization of natural resources, and to be based on the precautionary principal and on the principles that preventive action should be taken, environmental damage should, as a priority, be rectified at source and that the polluter should pay."

Policies differ globally (cont)

- Precautionary principle
  - "In order to protect the environment, the precautionary approach shall be widely applied by States according to their capabilities. Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation (Rio Convention !992)

Policies differ globally (cont)

- CCME guiding principles
  - "Guidelines are generic national recommendations that are based on the most current scientific information available at the time of their derivation (i.e., they do not directly consider site-specific, technological, socioeconomic, or management factors that may influence their implementation)."

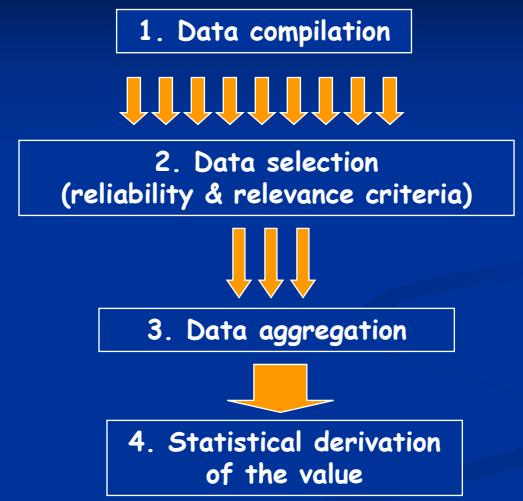
Policies differ globally (cont)

- CCME guiding principles
  - "Guidelines are meant to protect all forms of aquatic life and all aspects of the aquatic life cycles, including the most sensitive life stage of the most sensitive species over the long term, from the negative effects of anthropogenically altered environmental parameters (e.g., pH, temperature, and dissolved oxygen) or exposures to substances via the water column."

Policies differ globally (cont)

- USEPA
  - Contains many "precautionary elements" but does not adhere to the precautionary principle. Other factors, including economic considerations, are considered in US environmental policy.
  - US policy does not attempt to protect all forms of aquatic life and all aspects of the aquatic life cycles at all times but does consider "important species."

All derivation methods are remarkably similar



Areas where methods differ

- Guiding principles
  - Protecting all organisms in all waters at all times…
  - Acute vs chronic criteria
- Data used for derivation
  - What species are to be considered in the database? (How many and which ones)
  - What types of data are used?
    - Endpoints (survival, growth, reproduction, other)
    - Statistical endpoints (EC10, EC20, MATC, NOEC, LOEC)
    - Relevance and reliability assessment

Areas where method differ

- Statistical methodology used to derive criteria
  - Log triangular distribution
  - Log normal distribution
  - Best fit approach
  - Burr III distribution

General EU-based framework

PNEC derivation

Algae/invertebrates /fish

Bacteria/ protozoa

Sediment dwelling organisms

Bacteria/plants/ invertebrates

Micro-organisms in STP

Aquatic ecosystem

Sediment ecosystem

Terrestrial ecosystem

Reference value derivation

General EU framework

1. Data compilation

2. Data selection (reliability & relevance criteria)

3. Data aggregation

4. Reference Value & PNEC derivation

PNEC derivation-chronic exposure

water

Ideally the SSD should cover at least 8 taxonomic groups containing at least 10 NOECs (preferably more than 15) for different species (London workshop, 2001).

	Taxonomic Groups
1	Fish (usually tested species like trout, bluegill, channel catfish etc.)
2	A 2nd family in the Phylum Chordata (e.g., fish, amphibian, etc)
3	A crustacean (e.g., cladoceran, copepod, ostracod, isopod, amphipod, crayfish, etc.)
4	An insect (e.g., mayfly, dragonfly, damselfly, stonefly, caddisfly, mosquito, midge, etc.)
5	A family in a phylum other than Arthropoda or Chordata (e.g., Rotifera, Annelida, Mollusca, etc.)
6	A family in any order of insects or any phylum not already represented
7	Algae
8	Higher plants

Data requirements

- Only chronic standards are developed, therefore only chronic tests are considered.
  - Data requirements are "looser" than in the US.
- Data endpoints are EC10 or NOEC.

Data aggregation

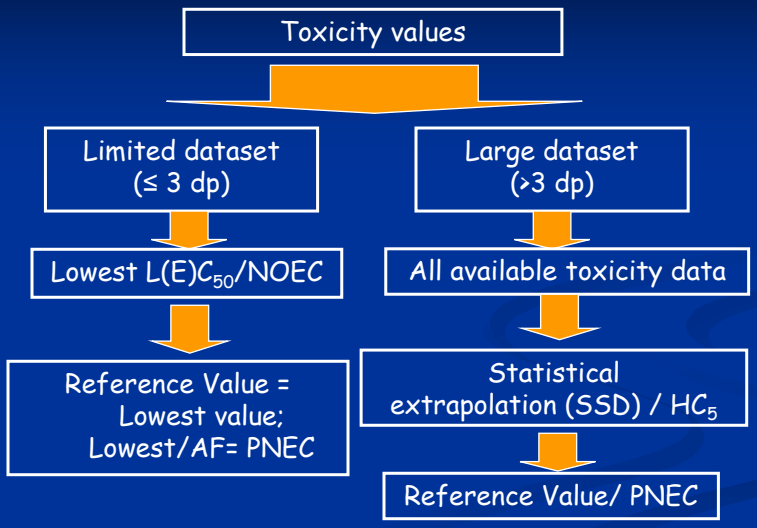
1. Grouping of data
   - grouping per species/endpoint
   - grouping according to region specific boundaries of physico-chemical properties (or normalized using bioavailability models)

2. Geometric mean (# > 2 dp)

3. Lowest value based on different endpoints

4. Most sensitive life stage

Reference Value/PNEC derivation



PNEC derivation - chronic exposure

1. Data poor substances
   - Additional testing or
   - Use of empirically derived assessment factors on the lowest acute/chronic value

Available data	Assessment factor
At least one short-term L(E)C_{50} from each of three trophic levels of the base set (fish, Daphnia and algae)	1,000[a]
One long-term NOEC (either fish or Daphnia)	100[b]
Two long-term NOECs from species representing two trophic levels (fish and/or Daphnia and/or algae)	50[c]
Long-term NOECs from at least three species (normally fish, Daphnia and algae) representing three trophic levels	10[d]

Test Species Requirements

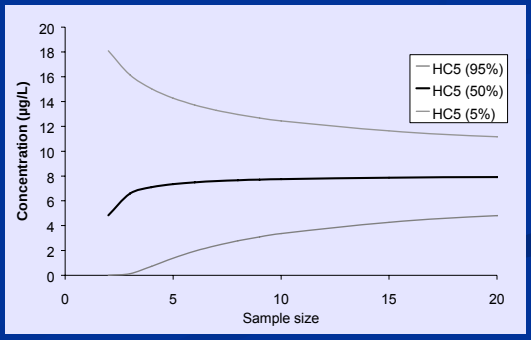
US EPA	EU
the family Salmonidae in the Class Osteichthyes	Fish
A second family of fish in the Class Osteichthyes (preferably a commercially or recreationally important warm-water species)	Second family in the phylum Chordata
A third family in the phylum Chordata	
Planktonic crustacean	Crustacean
Insect	Insect
A family in a phylum other than Arthropoda or Chordata	A family in a phylum other than Arthropoda or Chordata
A family in any order of insect, or any phylum not already represented	A family in any order of insect of any phylum not already represented
Benthic crustacean	
	Algae
	Higher plant

PNEC derivation - chronic exposure

2. Data rich substances
- Use of statistical extrapolation method (with bioavailability correction)
- Both parametric and non-parametric distributions could be used
- Impossible to exclude *a priori* any distribution however, log normal or log logistic approach is "strongly" recommended:
  - www.rivm.nl/bibliotheek/rapporten/601501028.html
- Carefully evaluation of goodness-of-fit (preference to A/D tests)
- PNEC = 5th % of SSD

PNEC derivation - chronic exposure

2. Data rich substances
- Use of statistical extrapolation method (with bioavailability correction)
  - At least 4 datapoints
  - The more data points the more precise the HC_5 will be
  - Should include the appropriate taxonomic groups/trophic levels



Elements of an AWQC

- Concentration of Exposure: How much – aka: **Magnitude**
- ~~Time Period of Exposure: How long – aka: **Duration**~~
  - Acute (1 hr avg) & Chronic (4 day avg)
- ~~Frequency of Exposure: How often – aka: **Frequency**~~
  - ~~1x every three years on average~~

Canadian Water Quality Criteria Framework

Draft Guideline released Summer 2007

Two types of criteria

- Long-term exposure guidelines identify benchmarks that are intended to protect all forms of aquatic life (all species, all life stages) for indefinite exposure periods.
- Short-term exposure guidelines identify benchmarks that protect only a specified fraction of individuals from severe effects such as lethality for a defined short-term exposure period.

Criteria Application

- A guideline generally refers to the **total** concentration of the substance in an unfiltered sample. Total concentrations will apply unless it can be demonstrated that
  - the relationship between variable fractions and their toxicity is firmly established and
  - analytical techniques have been developed that unequivocally identify the toxic fraction of a variable in a consistent manner using routine field-verified measurements.

Separate freshwater and marine criteria

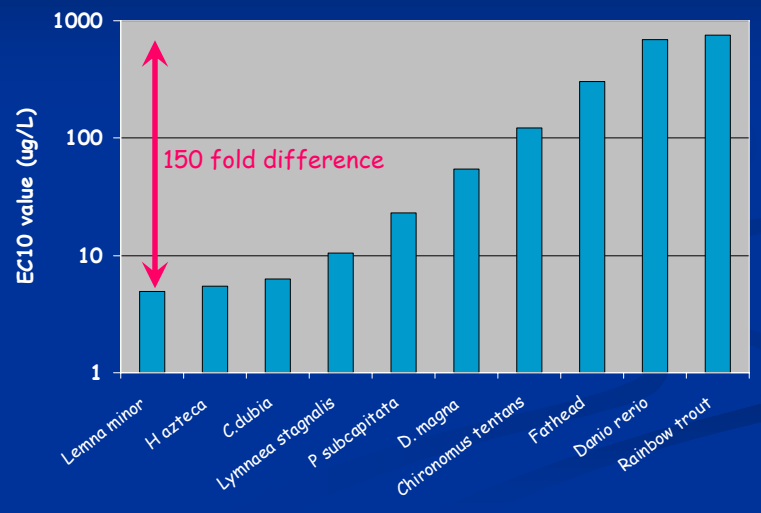
- Guidelines are set separately for freshwater and marine systems.
  - Freshwater is defined as water with total dissolved salt content equal to or lower than 1000 ppm (1 g×L-1, 10/00 [parts per thousand]).
  - Marine water is defined as water with total dissolved salt concentration greater than 5000 ppm (5 g×L-1, 50/00).
  - In brackish water (TDS 1–50/00), the water quality guideline protecting the most sensitive condition (freshwater or marine) should be applied, unless sufficient data are available on resident aquatic species and environmental conditions to justify a different choice.

Three types of criteria

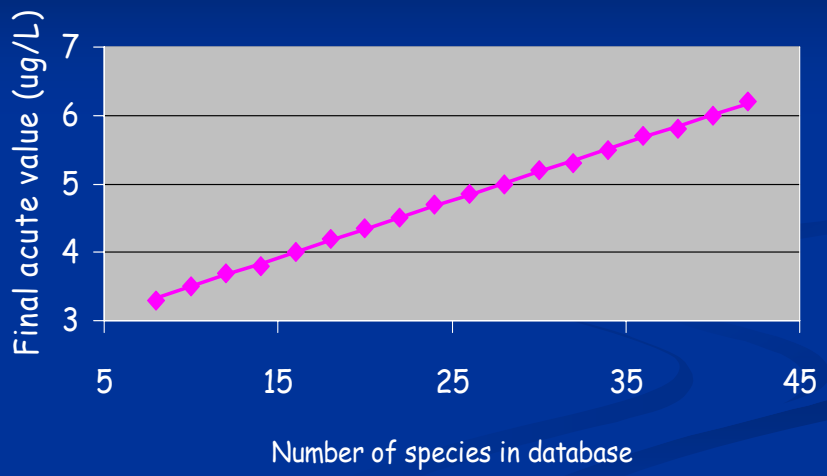
- Type A guidelines are derived using a species sensitivity distribution (SSD) approach when there are adequate primary and secondary toxicity data to satisfactorily fit a SSD curve.
- Type B guidelines are derived for substances that either have inadequate or insufficient toxicity data for the SSD approach, but for which enough toxicity data from a minimum number of primary and/or secondary studies are available.
  - Type B guidelines are divided into Type B1 and Type B2 guidelines, based on the quantity and quality of available toxicity data.

Lets take a look at the SSD fitting procedures

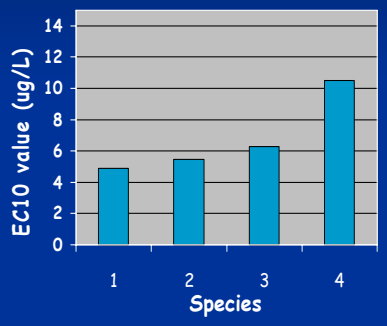
Example Data Set



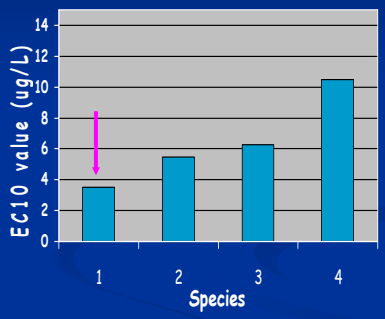
FAV calculations are sensitive to database parameters



Data relationships will effect FAV values

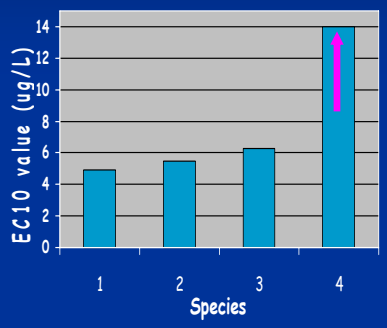


FAV 3.3 ug/L

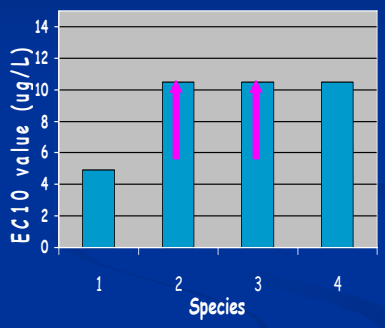


FAV 2.4 ug/L

Data relationships will effect FAV

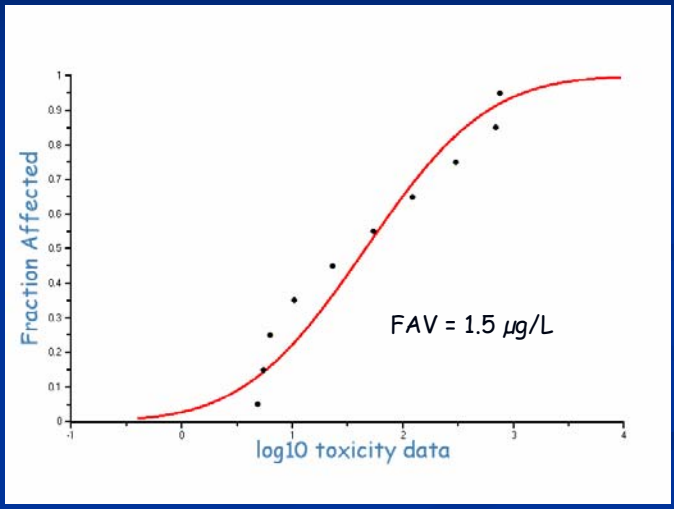


FAV 3.13 ug/L

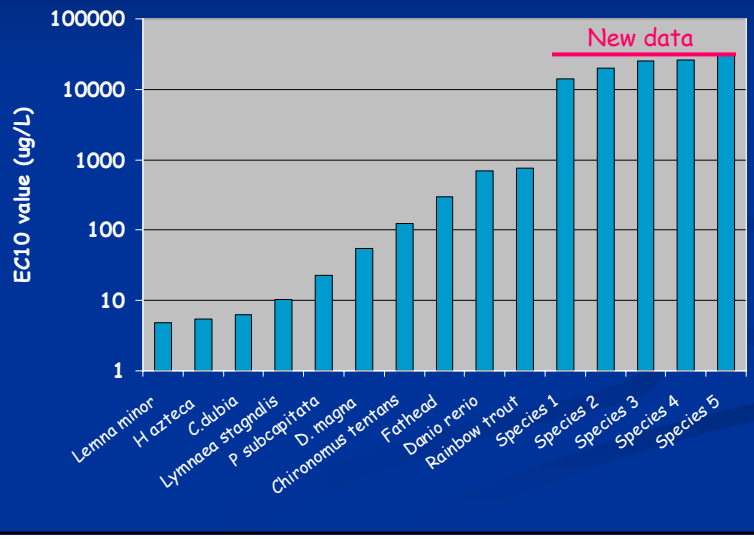


FAV 4.0 ug/L

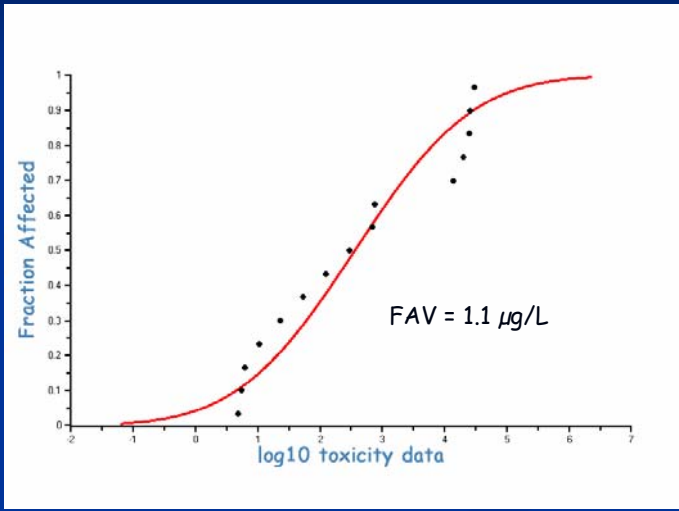
Results using RIVM ETX



Example Data Set



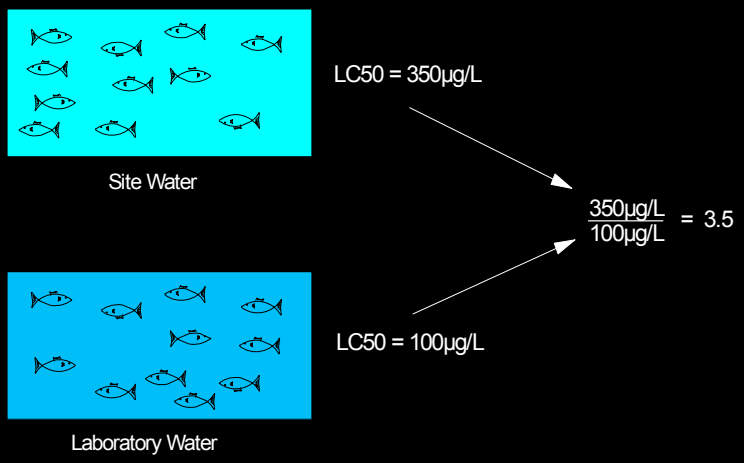
Results using RIVM ETX



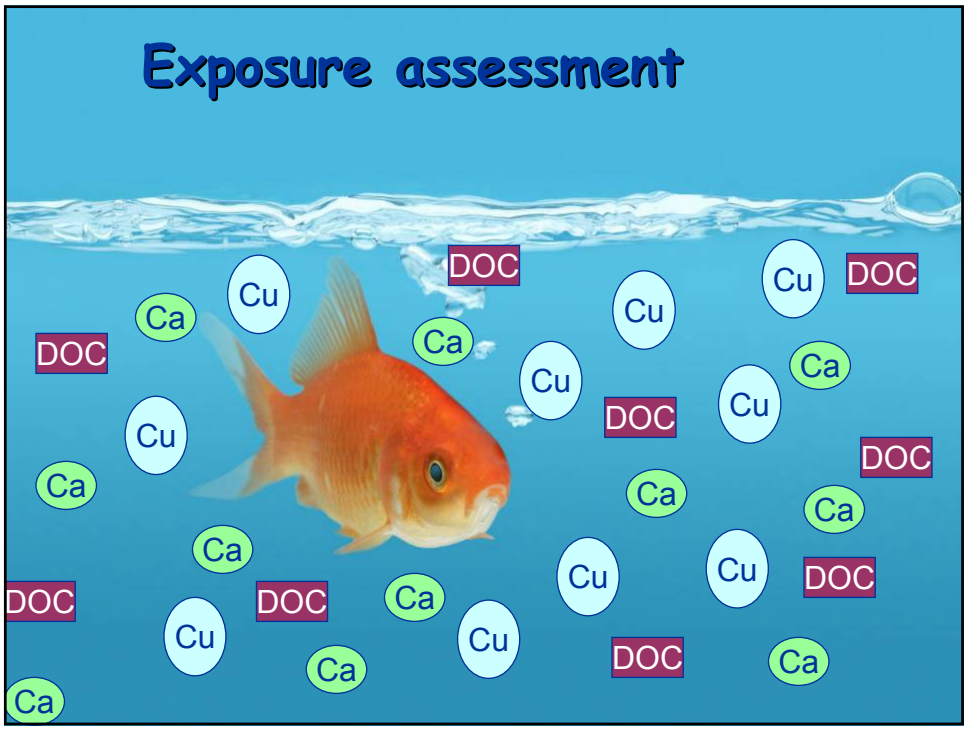
Biotic Ligand Models

An implementation nightmare?

Reality raises its ugly head!



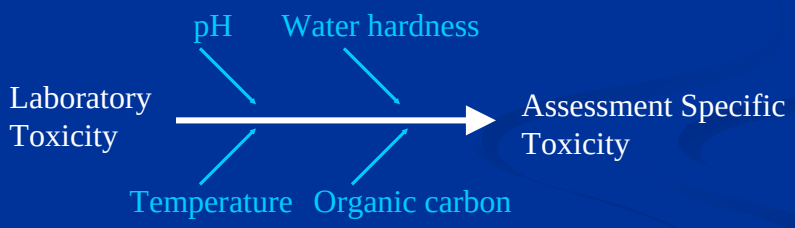
Exposure assessment



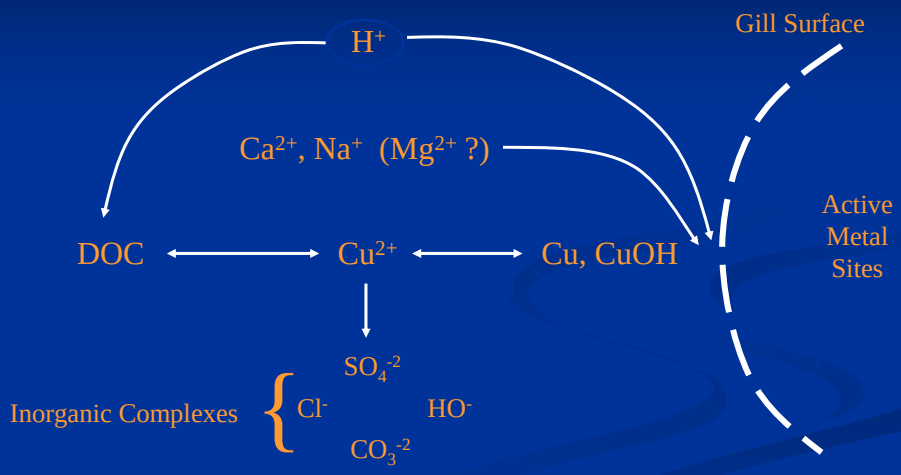
Site Specificity and Bioavailability

- Chemistry Matters
  - The physical/chemical characteristics of the site alter the bioavailability/toxicity of the pollutant
  - DOC, Hardness, pH, BLM, WER
- Biology Matters
  - The sensitivities of the site-species differ from the national data base
  - Recalculation procedure

Mechanistic models must be used to predict toxicity



BLM Basis



[DiToro, 2000]

Freshwater AWQC using Hardness

Cd Criteria Equation* = $e^{(1.0166\ (\ln \text{Hardness}) - 3.924)}$

Hardness (mg/L)	Equation	Criteria Value (µg/L)
50	$e^{(1.0166\ (\ln 50) - 3.924)}$	1.1
100	$e^{(1.0166\ (\ln 100) - 3.924)}$	2.1
200	$e^{(1.0166\ (\ln 200) - 3.924}$	4.3

* Based on total recoverable metal

Comparison of CMC Calculated by BLM or Hardness Equation [from 2007 Copper Criteria Update]

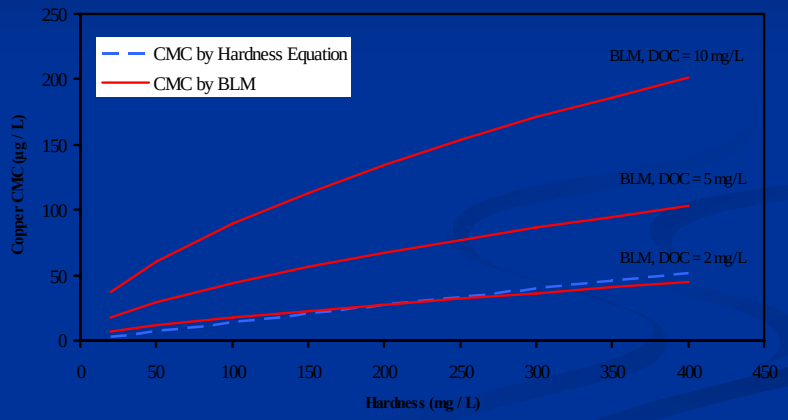


Figure 5. Comparison of CMC calculated by BLM or Hardness Equation Alkalinity (11 - 245 mg CaCO3/L) and pH (7.3 - 8.7) Covary with Hardness

Appendix G: Representative water quality criteria values using the BLM and the Hardness equation approaches for waters with a range in pH, Hardness, and DOC concentrations. The BLM calculation assumed that alkalinity was correlated with pH, and that other major ions were correlated with hardness based on observed correlations in EPA synthetic water recipes.

pH	Hardness	DOC	Hardness Equation Based Water Quality Criterion for Cu[1]	BLM Based Instantaneous Water Quality Criterion for Cu
	mg/L $CaCO_3$	mg / L	µg / L	µg / L
6.5	40	2	5.9	1.6
		4	5.9	3.3
		8	5.9	6.8
		16	5.9	14.3
	80	2	11.3	1.9
		4	11.3	3.8
		8	11.3	7.7
		16	11.3	16.0
	159	2	21.7	2.3
		4	21.7	4.5
		8	21.7	9.2
		16	21.7	18.9
	317	2	41.5	2.8
		4	41.5	5.6
		8	41.5	11.4
		16	41.5	23.1
7.0	40	2	5.9	3.9
		4	5.9	8.0
		8	5.9	16.4
		16	5.9	34.3
	80	2	11.3	4.4
		4	11.3	8.8
		8	11.3	18.0
		16	11.3	37.0
	159	2	21.7	5.1
		4	21.7	10.3
		8	21.7	20.7
		16	21.7	42.4
	317	2	41.5	6.2
		4	41.5	12.4
		8	41.5	24.9
		16	41.5	50.6

REACH

Registration, Evaluation and Assessment of Chemicals

Registration

- all chemicals produced or imported in volumes higher than one ton per year and per manufacturer or importer will have to be registered
- 5 types of information required
  - properties
  - intended uses
  - likely exposure scenarios
  - potential risks to human health and the environment
  - how the risks will be managed

Evaluation

- all chemicals produced or imported in volumes higher than one hundred tons per year and per manufacturer or importer and those that give rise to concern will have to be evaluated
- risk assessment will be required
- development of additional testing programmes for chronic effects

Authorization

- Will be required for substances of very high concern, that is those which are
  - CMRs
  - PBTs
  - vPvBs
  - endocrine disrupters
  - substances of an equivalent level of concern, for example POPs
- Separate approval required for each of the uses of a chemical

A few examples

Cobalt and Manganese

Cobalt: Application of an International Approach for Developing Aquatic Criteria/Guidelines/Standards for Metals

Program Background

- No AWQC or PNEC exist for Cobalt
- In comparison to other metals, relatively few data exist for cobalt
- Extant data suggests water hardness may have a profound effect on Co acute and chronic toxicity. Possible effects of other factors such as pH, alkalinity and Natural Organic Matter (NOM) were unknown.

Program Objective

To develop the data necessary for derivation of:

- an EU predicted no effect concentration (PNEC) for cobalt and
- a US national ambient water quality criteria (AWQC).

Both efforts must consider the modifying effects of water quality parameters on Co toxicity, i.e., the Biotic Ligand model.

Study Approach

Three tiered experimental design:

- Tier 1: Range-finding/screening tests to identify those mitigating factors likely to effect Co toxicity
  - Existing studies did not always follow standard/acceptable protocols

Study Approach

- Three tiered experimental design:
  - Tier 1:Range-finding screening tests to identify those mitigating factors likely to effect Co toxicity and guide subsequent BLM efforts
  - Tier 2: Develop the acute effects data needed for a US EPA AWQC and to set exposure concentrations for chronic tests

Study Approach

- Three tiered experimental design:
  - Tier 1: Range-finding screening tests to identify those mitigating factors likely to effect Co toxicity and guide subsequent BLM efforts
  - Tier 2: Develop the acute effects data needed for an USEPA AWQC and to set exposure concentrations for chronic tests
  - Tier 3: Develop the chronic effects data needed for derivation of an EU PNEC.

Test program overview

EU Requirement	US EPA Requirement	Test Species	Test Method
Fish	the family Salmonidae in the Class Osteichthyes	Rainbow trout	Early Life-Stage
Second family in the phylum Chordata	A second family of fish in the Class Osteichthyes (preferably a commercially or recreationally important warm-water species)	Fathead minnow	Early Life-Stage
	A third family in the phylum Chordata	Zebrafish	Early Life-Stage
Crustacean	Planktonic crustacean	*Daphnia magna*	Life-Cycle (21d)
Insect	Insect	Chironomid	Life-Cycle

Test program overview

EU Requirement	US EPA Requirement	Test Species	Test Method
A family in a phylum other than Arthropoda or Chordata	A family in a phylum other than Arthropoda or Chordata	Caddisfly	Life-Cycle
A family in any order of insect of any phylum not already represented	A family in any order of insect, or any phylum not already represented.	Snail	Chronic (28d), Growth rate
	Benthic crustacean	*Hyalella azteca*	Chronic (28d), growth rate
Algae		*Pseudokirch neriella subcapitata*	Chronic (72h), growth rate
Higher plant		*Lemna minor*	Chronic (7d), growth rate

Test Procedures

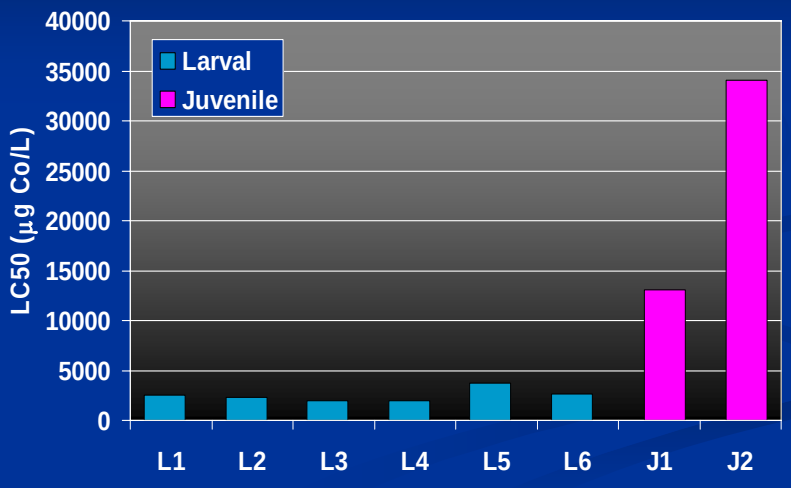
- All tests followed OECD, ASTM, EPA methods.
- Tests were conducted using flow-through methods where possible.
- All studies had measured exposure concentrations (dissolved Co)

Acute toxicity data for Cobalt

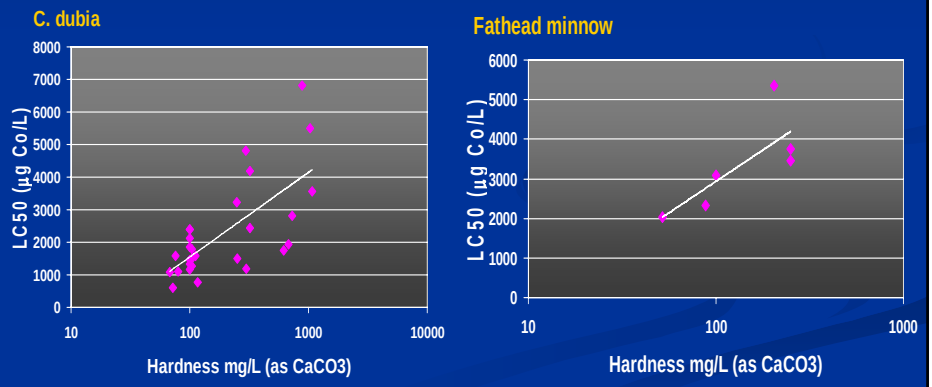
Species	LC50 (µg/L)
Rainbow trout	1147
Ceriodaphnia dubia	1921
Mottled Sculpin	2110
Fathead minnow	3172
Hyalella azteca	3290
Centroptilum conturbatum	3900
Daphnia magna	5917
Danio rerio	15980
Lymnaea stagnalis	61600
Seratella tibialis	79100
Crangonyx pseudogracilis	167000
Chironomus tentans	259425
Brachycentrys americansus	7219000

Note: Some data should be considered preliminary

Fathead Minnow Life-stage Sensitivity



Co Acute toxicity is affected by water hardness



Acute toxicity data for Cobalt

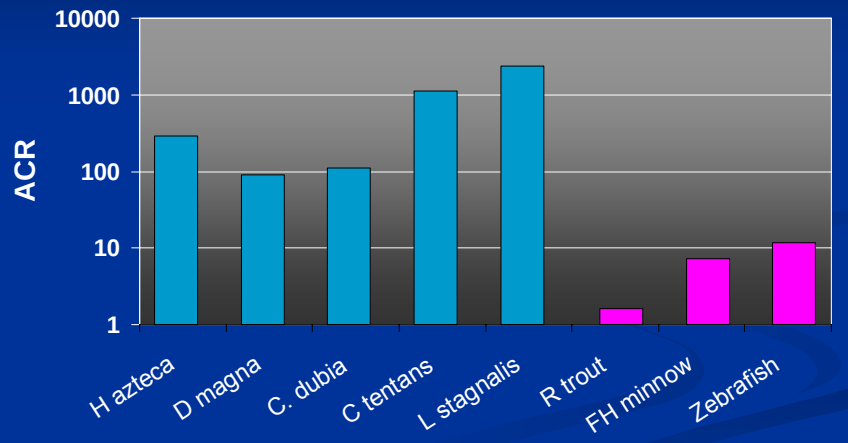
Species	LC50 (µg/L)	LC50 (µg/L) (@hardness of 50 mg/L)
Rainbow trout	1147	1226
Ceriodaphnia dubia	1921	1296
Mottled Sculpin	2110	2030
Fathead minnow	3172	2374
Hyalella azteca	3290	2513
Daphnia magna	5917	3689
Centroptilum conturbatum	3900	4260
Danio rerio	15980	13038
Lymnaea stagnalis	61600	45530
Seratella tibialis	79100	86411
Crangonyx pseudogracilis	167000	167000
Chironomus tentans	259425	251265
Brachycentrys americansus	7219000	7886251

Chronic toxicity data for Cobalt

Species	EC10 (µg/L)	EC20 (µg/L)	EC20 (µg/L) (@hard. of 50 mg/L)
Lemna minor	4.9	--	--
Hyalella azteca	5.5	11	8.8
Ceriodaphnia dubia	6.3	15	12
Lymnaea stagnalis	11	18	19
P. subcapatata	23	--	--
Daphnia magna	54	65	41
Chironomus tentans	123	205	224
Fathead minnow	301	463	326
Rainbow trout	691	997	771
Danio rerio	755	1393	1105

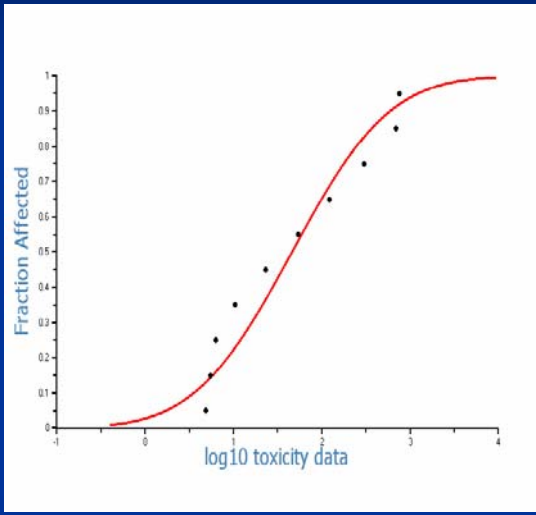
Note: Some data should be considered preliminary

Acute to Chronic Ratios



HC5 calculation

- Chronic data for 10 species available.
- EC10 values used.
- Lowest EC10 for *Lemna minor* (4.9 µg/L).
- Median HC5 = 1.54 µg/L (95% CI: 0.14-6.03)



Calculated using ETX 2.0 (RIVM 2004)

Chronic Criteria Calculation for Cobalt

Final Chronic Value (µg/L)	Equation	Hardness (mg/L as CaCO3)	Co (µg/L)
Using USEPA SSD approach	$e^{.2936(\text{Ln hardness})+0.3211}$	50	4.3
		100	5.3
		200	6.5
HC5			1.54

Conclusions

- Cobalt acute toxicity (LC50) ranges from ~1mg/l to more than 1 g/L.
  - No obvious sensitivity differences among organisms groups
- Co is substantially more toxic chronically (EC10: 5-755 µg/L)
  - Invertebrates appear more sensitive than fish
- Available data show that Co toxicity is affected by water quality parameters such as hardness and pH and may be affected by organic carbon concentrations.

Conclusions

- Biotic-ligand models are currently under development and will affect calculation of PNEC/AWQC values.
- PNEC/AWQC (chronic) values are likely to be in the low µg/L (1.5-7) range. Consideration of BLM parameters may well affect these values.
  - Background concentrations in European surface waters are estimated to be in the range of 0.18-0.21 µg/L.

Manganese

Literature Review

- More than 250 articles have been identified and retrieved
- Greater than 85% of those were rejected due to lack of relevancy, insufficient information on test conditions, poor test design (e.g., single dose level), statistics not used to derive toxicity values…

Review Status

Identified chronic exposure data - *water*

Taxonomic Group	Test Species	Reference
Fish	Rainbow Trout, Brook Trout, Brown Trout	Davies and Brinkman 1998; Goettl and Davies 1978; Lewis 1978; Stubblefield et al. 1997
Second family in phylum Chordata	Fathead Minnow	ENSR 1996
Crustacean	Ceriodaphnia dubia, Daphnia magna	ENSR 1989, 1992; Biesinger and Christensen 1972
Insect	—	—
Family in phylum other than Arthropoda or Chordata	—	—
Family in any order of insect or not already represented	—	—
Algae	—	—
Higher Plant	—	—

Identified acute exposure data - *water*

Taxonomic Group	Test Species	Reference
Family Salmonidae in the Class Osteichthyes	Rainbow Trout, Brook Trout, Brown Trout	ENSR 1990, 1994; Davies and Brinkman 1994, 1995, 1998
Second family of fish in the Class Osteichthyes	Fathead Minnow, Longfin Dace, Northern Squawfish	ENSR 1990, 1992, 1996; Lewis 1978, Beleau and Bartosz 1982
Third family in the phylum Chordata	Western Toad	ENSR 1996
Planktonic crustacean	Ceriodaphnia dubia, Daphnia magna	ENSR 1990, 1992; Biesinger and Christensen 1972; Lasier et al. 2000
Insect	Chironomus tentans	ENSR 1996
Family in a phylum other than Arthropoda or Chordata	Anodonta imbecillus	Wade et al. 1989
Family in any order of insect, or any phylum not already represented	—	—
Benthic crustacean	Hyalella azteca	ENSR 1996, Lasier et al. 2000; Borgmann et al. 2005

Summary of Acute-Chronic Ratio Data

Species	Water Hardness (as $CaCO_3$)	LC_{50} (µg Mn/L)	EC_{10} (µg Mn/L)	Acute/Chronic Ratio (ACR)	Genus Geometric Mean ACR
Fathead Minnow	30	8,557	2,289	3.7383	3.7383
Ceriodaphnia dubia	26	8,757	2,922	2.9969	
	50	12,513	4,370	2.8634	
	100	20,495	5,281	3.8809	
	200	25,480	6,910	3.6874	
	48	15,641	2,731	5.7272	3.7103
Daphnia magna	45	9,800	4,100	2.3902	2.3902
Brown Trout	48/31	15,973	4,330	3.6889	3.6889
Brook Trout	31	5,120	1,699	3.0135	
	150	27,500	2,826	9.7311	5.4156
Rainbow Trout	28	3,170	1,201	2.6395	
	150	16,200	3,477	4.6592	3.5064
Geometric Mean ACR					**3.6196**

Criteria for program selection

- Tiered assessment strategy
  - Identify/generate enough data to develop an acceptable answer (i.e., PNEC[NOEC*AF] > PEC)
    - AF vs. SSD approach
  - Will BLM approach help? (PNEC decreased based on bioavailability concerns)
- Internationally acceptable
  - Test results must be acceptable to **all** regulatory authorities.

Test program overview

US EPA Requirement	EU Requirement	Test Species	Chronic
the family Salmonidae in the Class Osteichthyes	Fish	Fathead minnow	ELS
A second family of fish in the Class Osteichthyes (preferably a commercially or recreationally important warm-water species	Second family in the phylum Chordata	Rainbow trout	ELS
A third family in the phylum Chordata		Medaka	ELS or EU juvenile growth
Planktonic crustacean	Crustacean	*Daphnia magna*	Life-cycle
Insect	Insect	Chironomid	Life-cycle
A family in a phylum other than Arthropoda or Chordata	A family in a phylum other than Arthropoda or Chordata	Caddisfly	Life-cycle
A family in any order of insect, or any phylum not already represented	A family in any order of insect of any phylum not already represented	Snail	Life-cycle
Benthic crustacean		*Hyalella azteca*	Life-cycle
	Algae	*Pseudokirchneriella subcapitata*	Life-cycle
	Higher plant	*Lemna*	Life-cycle

What does the future hold?

- New data will become available:
  - Old metals (Cu, Pb, Ni, Cd, Zn….)
  - New metals (Co, W, Mn, Au, Pt, Sn, …)
  - Organics (Emerging Chemicals)
- BLMs